

LASER-INDUCED FLUORESCENCE OF SPACE-EXPOSED POLYURETHANE

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SUMMARY

The objective of this work was to utilize laser-induced fluorescence techniques to characterize several samples of space-exposed polyurethane. These samples were flown on the Long Duration Exposure Facility (LDEF), which was in a shuttle-like orbit for nearly 6 years. Because of our present work to develop laser-induced-fluorescence inspection techniques for polymers (U.S. Patent No. 4,802,762), space-exposed samples and controls were lent to us for evaluation. These samples had been attached to the outer surface of LDEF; therefore, they were subjected to thermal cycling, solar ultraviolet radiation, vacuum, and atomic oxygen. It is well documented that atomic oxygen and ultraviolet exposure have detrimental effects on many polymers. This was a unique opportunity to make measurements on material that had been *naturally* degraded by an unusual environment. During our past work, data have come from *artificially* degraded samples and generally have demonstrated a correlation between laser-induced fluorescence and tensile strength or elasticity.

Laser-induced fluorescence techniques using 488-nm excitation (visible) were successfully used to inspect the space-exposed polyurethanes, with enhanced sensitivity over standard blacklight inspection. For example, degradation variations on absorptive (black) polyurethane samples could be observed. (Compared to ultraviolet excitation, visible-wavelength excitation techniques sometime reveal additional features, such as tensile strength degradation.) Anomalies between the control samples from LDEF integration and fresh samples were also observed. Laser-induced fluorescence techniques were also used together with video-imaging technology to reveal artifacts that may not have been detected with standard blacklight inspection. Effects that were slightly visible under standard blacklight inspection were more easily measured using laser-induced fluorescence because of the ease of handling the laser beam with fiber optics and the capability to increase the power density on the sample.

The laser-induced fluorescence technique has good potential for remote, nondestructive inspection of polymers. One future application may be remote sensing of polymer degradation from the space environment such as might occur on the outside of the space station or defense satellites. Another application may be in the laboratory for rapid inspection with enhanced sensitivity as compared to blacklight-inspection methods. Future work is needed to address the correlation between fluorescence intensity and degradation parameters, such as tensile strength or elasticity, for materials used in space applications.

TECHNICAL BACKGROUND

Laser-Induced Luminescence

Laser-induced luminescence (LIL) is emission of light resulting from absorption of laser energy by a substance. Re-radiated light contains a major component at the wavelength of the exciting laser light (reflected light); however, there are also many new wavelengths (luminescence) that are determined primarily by the electronic structure of the substance. Laser-induced luminescence includes both laser-induced fluorescence (LIF), which is fast luminescence occurring on time scales of the order of several nanoseconds, and laser-induced phosphorescence (LIP), which is slower luminescence occurring on time scales as long as several seconds. The luminescence spectrum is not only a function of time, but also a function of the excitation spectrum. Fluorescence and phosphorescence have been studied for a number of years and have been used in numerous ways in the laboratory environment. Laser-induced luminescence is finding widespread use in many new and diverse applications; for example, it is currently being used to measure polymer degradation (refs. 1–4), to detect fingerprints, and to map flowfields in chemical lasers. In recent years, advances in laser technology have increased reliability and portability of lasers and have also generally reduced costs.

In many applications, fluorescence dominates phosphorescence. Fluorescence is characterized by many spectra depending on the excitation wavelength. A fluorescent molecule emits a fluorescence spectrum after it absorbs radiation within its excitation spectrum. The spectral distribution of the fluorescent radiation is a physical and absolute characteristic of a given substance for a given excitation wavelength and is useful for qualitative considerations. Emission intensity of fluorescence at a given wavelength is useful for quantitative analysis with a given instrument after standardization. Quantitative measurements show that there is sometimes a very strong correlation between laser-induced luminescence and some physical characteristic of the material, such as tensile strength or elasticity; many times this is because fluorescence primarily reveals relationships between molecular functional groups, such as conjugation. Because relationships between certain molecular functional groups are altered during degradation, laser-induced luminescence can be used to monitor these processes.

With the monochromaticity and power density available from lasers, molecules can be probed that are not normally thought of as fluorescent. For instance, samples that exhibit ultraviolet absorption can sometimes be induced to fluoresce with laser excitation in the visible region of the spectrum. This effect can be very important from the viewpoint of practical implementation.

When laser-induced fluorescence is measured with a video camera or visually assessed using optical filters instead of a narrow-bandwidth spectrometer, fluorescence signals of several wavelengths are measured simultaneously. Laser-induced fluorescence measured in this fashion is referred to as "integrated fluorescence" because the signal is related to the integral of the fluorescent-light intensity, weighted by the filter-detector response, over the wavelengths to which the system responds. Hence,

$$I(\lambda_e) = \int LIF(\lambda_e, \lambda) D(\lambda) f(\lambda) d\lambda, \quad (1)$$

$I(\lambda_e)$ = integrated fluorescence for excitation wavelength λ_e

$LIF(\lambda_e, \lambda)$ = laser-induced fluorescence at wavelength λ when excited with wavelength λ_e

$D(\lambda)$ = detector response at wavelength λ

$f(\lambda)$ = filter response at wavelength λ .

Note that $LIF(\lambda_e, \lambda)$ is also a function of the penetration depths (absorption and scattering parameters) for both the excitation and detection wavelengths, as well as the quantum yield for fluorescence of the material.

Long Duration Exposure Facility

The LDEF was placed into orbit in April 1984 during Space Shuttle *Challenger* mission STS-41C (refs. 5–6). This 4.3-m×9.1-m (14-ft×30-ft), 9,979-kg (11-ton) satellite contained 57 international experiments which were designed to investigate effects of long exposure to the harsh space environment on electronics, optics, biological samples, and various materials that may ultimately be flown in space for long periods of time. In January 1990, LDEF was recovered by Space Shuttle *Columbia* during mission STS-32. LDEF was deployed at 475 km (295 miles) and retrieved at 330 km (205 miles).

Samples

It was reported that under blacklight (ultraviolet) illumination, some of the space-exposed polyurethane-based thermal control paint samples visibly fluoresced (ref. 7). From past experience (refs. 1–4), we know that laser-induced fluorescence can be used to give additional degradation information as compared to either blacklight fluorescence or visible reflectance. Boeing Defense and Space Group (Seattle, WA) lent us three samples of the space-exposed polyurethane so that we could experiment with our laser techniques on the samples. (The differences in fluorescence between ultraviolet and visible excitation form the basis for one of our patents in this field (ref. 1); therefore, some differences were expected.)

The three tray-clamp samples from the outside surface of LDEF were designated as DO4-6, HO9-11, and HO7-11. Each sample consists of a white (reflective) and black (absorptive) section, originally painted with ChemGlaze (manufactured by Lord Corp.) A276 reflective moisture-curing aliphatic (straight-chain structured) polyurethane and Z306 absorptive moisture curing aromatic (ring structured) polyurethane. One sample (HO7-11) has various levels of degradation due to “shadowing” effects. One of the samples (HO9-11) may be contaminated with silicone which out-gassed from another part of LDEF (ref. 8). A list of the samples is given in Table 1. The aluminum tray clamps were approximately 12.7 cm (5 in) in height and 5.1 cm (2 in) in width, with the polyurethane samples deposited as round discs on the tray clamps. The white (reflective) inner-disc

diameter was 3.2 cm (1.25 in) and the black (absorptive) outer-disc diameter was 4.4 cm (1.75 in). (Mounting holes were used as positional reference; thus when they were on the left, the 12 o'clock position corresponded to "up".)

LDEF was gravity-gradient stabilized so that one end was always pointed away from the Earth. Furthermore, LDEF did not spin and so the exposed samples had well defined positions and orientations with respect to outer space and the spacecraft motion. Therefore, various samples were exposed to different levels of atomic oxygen fluence, etc.

APPARATUS AND PROCEDURES

Spectral Measurements

The following describes the laboratory apparatus and procedures used to make the experimental laser-induced fluorescence spectral measurements. A schematic diagram of the apparatus is shown in Figure 1.

Excitation Source

A Spectra Physics model 2025-005 argon-ion laser operating at 488 nm was used as the excitation source. For measurements described in this report, the "constant-light output" mode was utilized so that drifts in output power were negligible. Laser plasma-discharge lines were removed from the beam with an Edmund Scientific P/N 03907 interference filter with central passband centered at 488 nm ("F1" in the figure). The beam was directed with front-surface turning mirrors so that it hit the sample at a 180° angle with respect to the detection axis. The beam was unfocussed and had a spot size approximately 2 mm in diameter where it hit the sample. Laser power at the sample was 28.4 mW measured using an Eppley thermopile. Laser power was constant for both the white and black samples so comparisons could be made. In future measurements, higher power or longer integration times will be used on the dark samples to increase the signal-to-noise ratio.

Collection Optics

Light was collected with a simple f/2.25 lens arrangement. Scattered laser light was filtered from the fluorescence using a 3-mm thick piece of Schott OG530 glass ("F2" in the figure). For these measurements, alignment and matching into the spectrometer were not critical because the fluorescence was relatively intense. (Fluorescence could be easily seen with the unaided eye when viewed through a OG530 filter or argon-ion laser safety goggles.)

Spectrometer System

A Jarrell-Ash 0.275-m spectrometer (f/3.8) with a 150 groove/mm grating and a 25-micron wide slit was used to disperse the light. This is the front-end to an EG&G/PAR optical multichannel analyzer (OMA) system. The detector was a model 1455R-700-HQ microchannel-plate (MCP) intensified diode array. The multi-alkali photocathode has a nominal "S1" response (200–900 nm). It was operated with a Peltier cooler (5° C) and the MCP gain set at 70 percent of maximum. Typical

OMS settings were: 30 ms/scan and 100 scans (accumulated). Spectra were digitally stored on 5.25-inch floppy disks for subsequent analysis. Typical spectra show a rapid fall-off of the response at approximately 750 nm and longer wavelengths which was an instrumental artifact caused by physical blockage of the diode array in the present mounting configuration. (Note that the fall-off of response below 530 nm is due to the Schott glass OG530 blocking filter.) Wavelength calibrations were routinely made against a low-pressure mercury discharge.

Imagery

The video set-up is depicted in Figure 2; details are as follows.

Excitation Source

The argon-ion laser described above was also used as the source for the imagery experiments. In this case, the 488-nm light was directed at the samples through a multimode, multi-stranded fiber-optic bundle ("FO" in the figure). This bundle served the purpose of scrambling the coherence of the beam so that interference fringes would not be superimposed on the images. The beam intensity at the sample surface was approximately 11 mW/cm².

Collection Optics and Processor

A Sony model XC-57/HV solid-state monochrome camera was used to image the sample ("C" in the figure). This camera had a macro-zoom lens (Computar LMZ45C5, "L" in the figure), internal infrared-cut filter, and an external 3-mm thick Schott OG530 glass laser-blocking filter ("F" in the figure). The image was captured with an Imaging Technology, Inc., model VP1100 overlay frame grabber installed in a Compaq DeskPro 486/33M personal computer, running Optimas 3.01 (written by Bioscan, Inc.) image-analysis software. Parameters were set so that the system response was linear over the range of interest. Images were analyzed, but not enhanced using the software.

Ultraviolet Inspection

Because blacklight ultraviolet inspection has been used extensively in the past, we also inspected these samples under blacklight. The source that was used was a Spectroline model MB-100 High Intensity Blacklight Lamp (365 nm); this is an industrial grade inspection unit (115 VAC at 3.3 amps). Under this excitation, the 3 o'clock portion of H07-11 showed up as brighter than the rest; H07-11 and D04-06 appeared about the same, but not too fluorescent.

Additionally, a helium-cadmium laser (Omnichrome model 56-XL) which produces approximately 15 mW over a 2-mm spot diameter at 325 nm was used to visually inspect the samples. In this mode, the silicon contamination on the aluminum part of the H09-11 tray clamp was apparent in the area near the middle mounting hole.

DATA AND RESULTS

Specific Experiments

Selected measurements will be discussed in the following. Care must be exercised in comparing spectra between different experiments as the detailed experimental parameters may have been slightly different. If curves are on the same graph, however, they were taken under identical circumstances and can therefore be compared. Additional data is given elsewhere (ref. 9).

Comparative Data on Same Sample

Typical laser-induced fluorescence spectra are shown in Figure 3. In this figure, spectra from the reflective (white) portion of sample H07-11 is shown from three different locations, i.e. 1 mm into the 3 o'clock position (upper curve), center, and 1 mm into the 9 o'clock position (lower curve). Under visible room light examination, this sample shows degradation, with the 9 o'clock area darkened. Figure 4 shows laser-induced fluorescence spectra from the same tray clamp, but on the absorptive (black) portion. Large differences can be easily seen between the two spectra, the upper curve from the 3 o'clock position and the lower curve from the 9 o'clock position. The differences could be detected under standard blacklight-inspection for the white portions, but not for the black portions. Laser-induced fluorescence differences can also be detected on the other samples, but are much smaller, typically less than 15 percent or less.

Comparison Between Samples

Figure 5 shows the laser-induced fluorescence spectra from the center of the three samples; with the most fluorescence from H07-11, decreasing with D04-06, and H09-11 respectively.

Comparison Between Control Samples from LDEF Integration and Fresh Samples

Significant differences were found when comparing the control samples from LDEF integration and sample D04-06. Two significant differences are present for both the reflective and absorptive polyurethane. (1) The control samples fluoresce more than the space-exposed samples in the 550-nm wavelength region. (2) There is more fluorescence in the red wavelength region (650 nm and longer) for the space-exposed samples. This unexpected result led us to investigate the control samples in greater detail. Differences between the spectra from the control samples and fresh samples, which were obtained in early 1992 from Lord Corporation, were also found. For both the reflective and absorptive polyurethanes, the fresh paint fluoresces significantly less than the LDEF-integration control samples. This could be because the details of the formulation have been changed since the control samples were made (ca. 1983), or the control samples have actually aged during storage or degraded in some way. These control samples did not go into space, so they are not contaminated with silicon, or other space debris.

Video and Digital Image Analysis

Figure 6 shows the laser-induced fluorescence digital photograph of sample H07-11. The top part of the picture corresponds to the 9 o'clock position on the sample. The brightness (offset) has been adjusted so that the fluorescence from the absorptive portion does not show up in this

presentation. Figure 7 is a graph of the luminance value along a vertical line from the 9 o'clock position (on the sample) to the 3 o'clock position (on the sample) taken from the digital information contained in Figure 6. Note that the fluorescence spectra shows much structure and a possible micro-cracking effect.

Microscopy

The saturated (overexposed) portion of Figure 6 was examined further. Under 40× macroscopic examination, it appears as a small impact crater with observable polyurethane displacement. Because of its intense fluorescence, it was possible to examine it under a standard fluorescence microscope (Polyvar MET, 40×). It appears to be some sort of fibrous material. Because of the apparent impact crater, it is believed that this contamination is space debris of some kind. (Destructive examination to determine the exact nature of this material was beyond the scope of this investigation.)

Summary

- Laser-induced fluorescence techniques were used to inspect the space-exposed polyurethanes, with enhanced sensitivity over standard blacklight inspection.
- Degradation of absorptive (black) polyurethanes was also observed using laser-induced fluorescence techniques.
- Fresh samples (1992) of the A276 and Z306 polyurethane (manufactured by Lord Corp.) do not fluoresce nearly as much as the LDEF-integration control samples.
- Increases or decreases in the 488-nm excited laser-induced fluorescence of the polyurethane with degradation depends upon the wavelength region of the fluorescence.
- Laser-induced fluorescence techniques, when using 488-nm excitation, may not be affected by some contaminants, because they are basically transparent at that excitation wavelength.
- Laser-induced fluorescence techniques can be used with video imaging technology to reveal artifacts that may not be revealed with standard blacklight inspection, such as the subtle differences between samples H09-11 and D04-06. The capability for real-time assessment of the validity of the data is a very valuable advantage. (Overexposures or underexposures can be immediately noticed and compensated for.)
- Effects that were slightly visible under standard blacklight inspection are more easily extracted using laser-induced fluorescence because of the ease of handling the laser beam with fiber optics and capability to increase the power density on the sample.

DISCUSSION

Space degradation of polymer materials is a very complex process. The A276 white polyurethane paint darkened during ultraviolet exposure (ref. 7); however, for some samples the atomic oxygen fluence was sufficient to "scrub" (oxidize and remove) the damaged resin from the surface. In some cases this left behind a fragile agglomeration of pigment particles that displayed optical properties similar to those of the original material. Presently, all the processes are not completely understood, although it is clear that polymers and organic binders involved are attacked (refs. 10-11).

Laser-induced fluorescence can be used to monitor and/or study some of these processes. More work is needed to correlate fluorescence with the degree of degradation of the tensile strength, for instance, for these particular materials. The technique has good potential for remote, non-destructive inspection of polymers. One future application may be remote sensing of polymer degradation from the space environment such as may occur on the outside of the space station or defense satellites. Another application may be in the laboratory for rapid inspection with enhanced sensitivity as compared to blacklight-inspection methods.

ACKNOWLEDGMENTS

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REFERENCES

1. Hill, Ralph H., Jr.: "Optical Inspection of Polymer-Based Materials," U.S. Patent No. 4,802,762, February 7, 1989.
2. Hill, R.H., Jr.: "Laser-Induced Fluorescence Inspection of Polyurethane and Related Materials," Final Report/Phase 1, SwRI Project No. 17-7958-828, November 15, 1988.
3. Hill, R.H., Jr., and Feuer, H.O., Jr.: "Laser-Induced Fluorescence Inspection of Polyurethane," *Proceedings of the 17th Symposium on Nondestructive Evaluation*, San Antonio, TX, April 17-20, 1989.
4. Hill, R.H., Jr.: "Laser-Induced-Fluorescence Analytical Technologies-Phase II," Interim Report BFLRF No. 276; ADA 248486, Contract DAAK70-87-C-0043, September 1991.
5. Photos of LDEF Retrieval Reveal Condition of Experimental Panels, *Aviation Week and Space Technology*, January 29, 1990, pp. 64-65.
6. Canby, Thomas Y.; and Schneeberger, Jon: "Satellite Rescue," *National Geographic*, vol. 180, no. 5, November 1991, pp. 106-130.

7. Golden, J.L.: "Thermal Control Materials," *LDEF Spaceflight Environmental Effects Newsletter*, vol. II, No. 3, June 15, 1991, pp. 17–18.
8. Golden, John: Boeing Defense and Space Group, private communication, October 31, 1991.
9. Hill, Ralph H., Jr.: "Laser-Induced Fluorescence of Space Exposed Polyurethane," Final Report SwRI Project 15-9682, April 6, 1992. (Available upon request from the author.)
10. Bohnhoff-Hlavacek, G.; et al.: *LDEF Spaceflight Environmental Effects Newsletter*, vol. II, No. 8, January 15, 1992. (Summary of the LDEF Materials Workshop 1991.)
11. Hamid, S.H., Amin, M.B., and Maadhah, A.G., eds.: *Handbook of Polymer Degradation*. Marcel Dekker, Inc., 1992.

Table 1. Samples (LDEF samples, material data, and preliminary fluence and exposure data supplied by Boeing Defense and Space Group, Seattle, WA. Fresh samples and data sheets were supplied by Lord Corp., Saegertown, PA).

Sample Designation	Comments	Absorbance/Emittance (for white samples)	Atomic Oxygen Fluence (atoms/cm ²)	Ultraviolet Exposure (ESH Units)
H07-11	Space end (visible degradation; in room light, visibly darker toward the 9 o'clock position)	0.61	4.27×10^{20} (at incident angle of 91°)	14,500
H09-11	Space end (near silicone coated reflector, slightly contaminated)	0.70	4.27×10^{20} (at incident angle of 91°)	14,500
D04-06	Side tray	0.64	2.56×10^8 (at incident angle of 143°)	9,400
Control	Left over from LDEF integration	N/A	N/A	N/A
Fresh Samples	Jan. 1992.	0.23/0.90 = 0.26 (from data sheet)	N/A	N/A

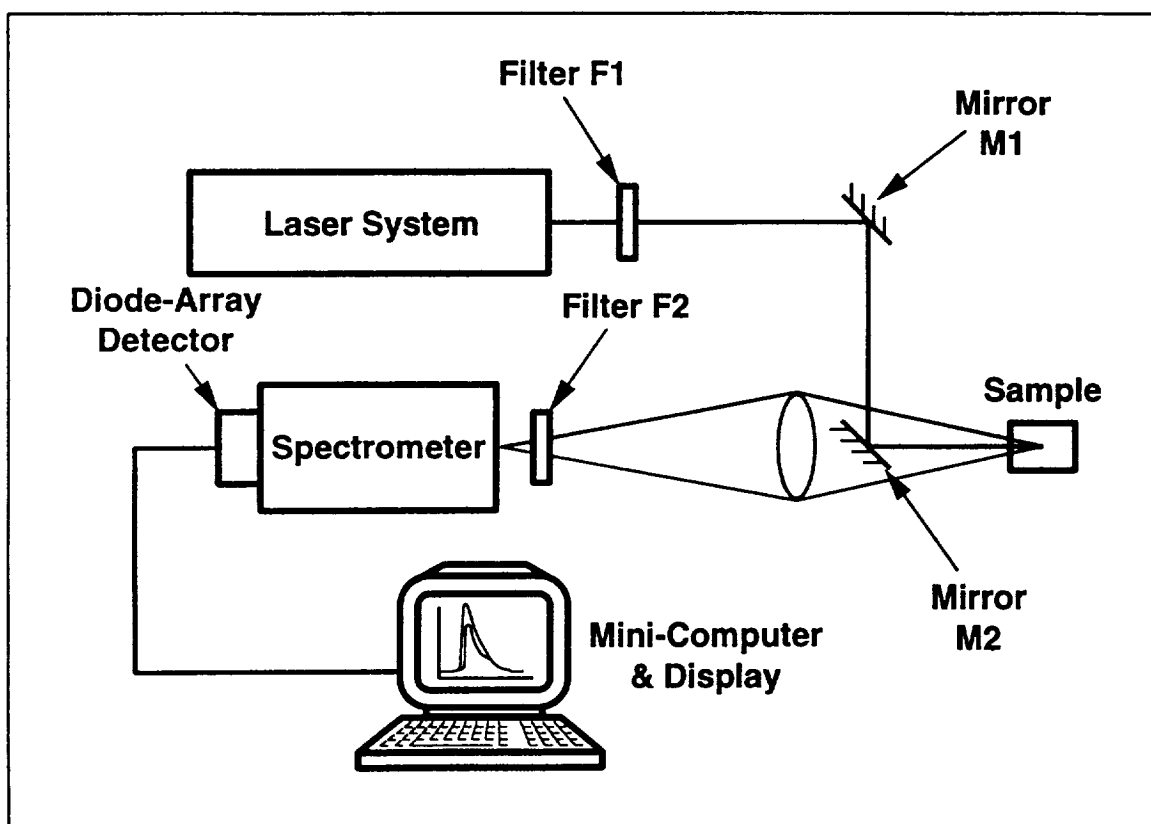


Figure 1. Experimental apparatus for spectral measurements.

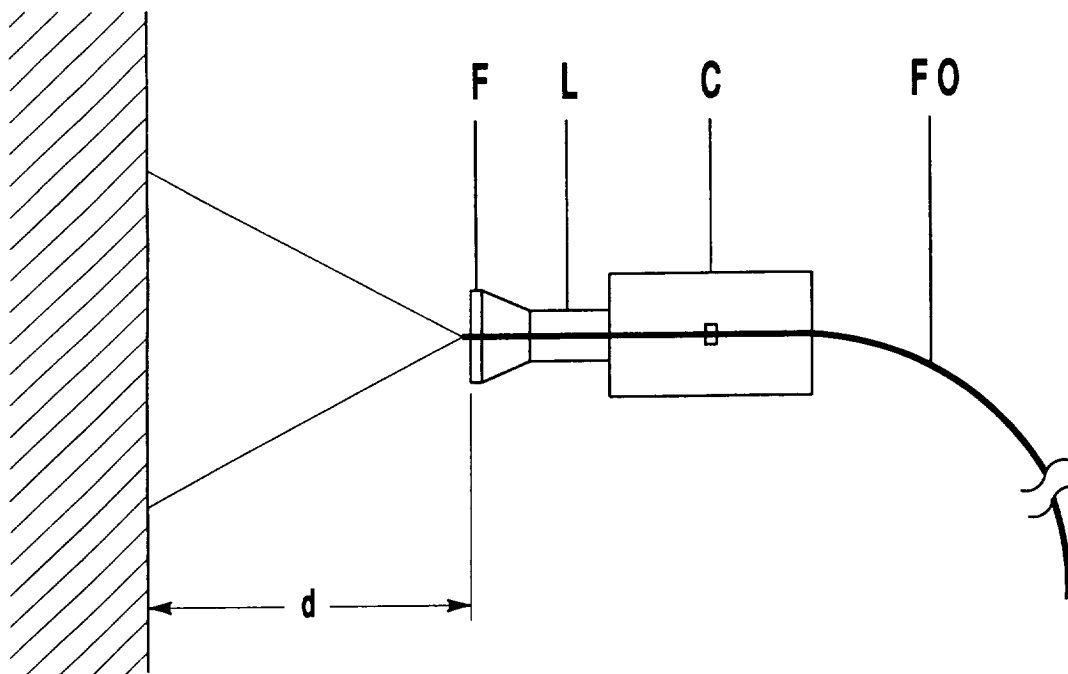


Figure 2. Experimental apparatus for video imaging. ("F" is the laser-blocking filter, "L" is the macro-zoom lens, "C" is the camera, "FO" is the fiber-optics bundle, and "d" is the standoff distance to the sample.)

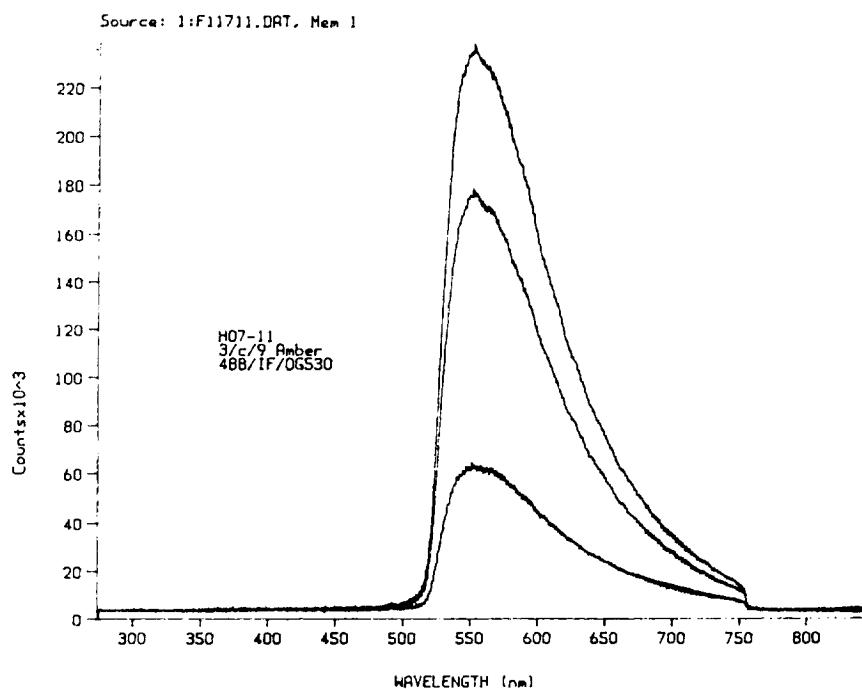


Figure 3. Laser-induced fluorescence spectra from the center reflective portion of H07-11. (Upper curve is from the 3 o'clock position, middle curve is from the central position, lower curve is from the 9 o'clock position.)

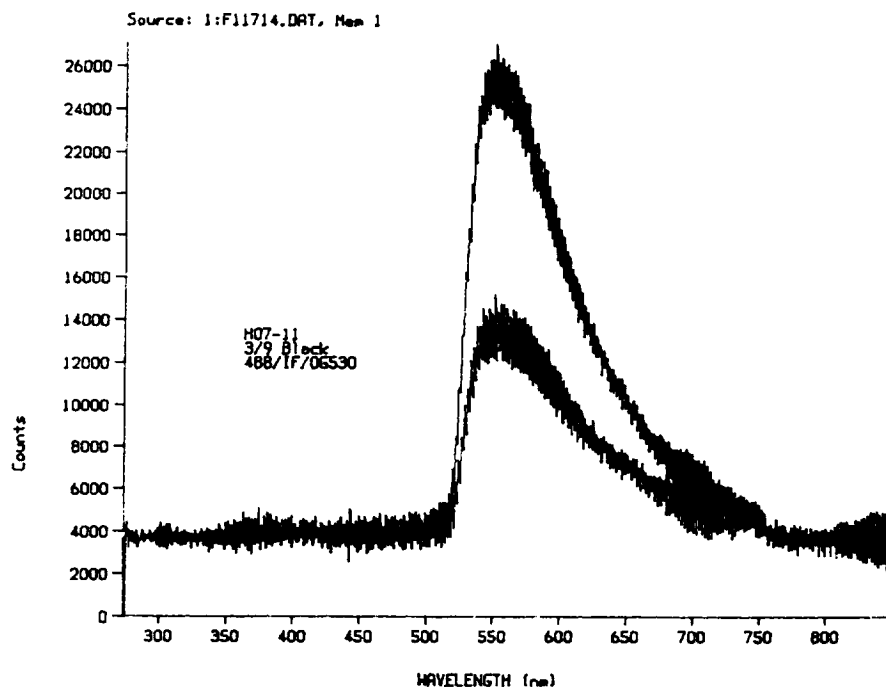


Figure 4. Laser-induced fluorescence spectra from the absorptive portion of H07-11. (Upper curve is from the 3 o'clock position, lower curve is from the 9 o'clock position.)

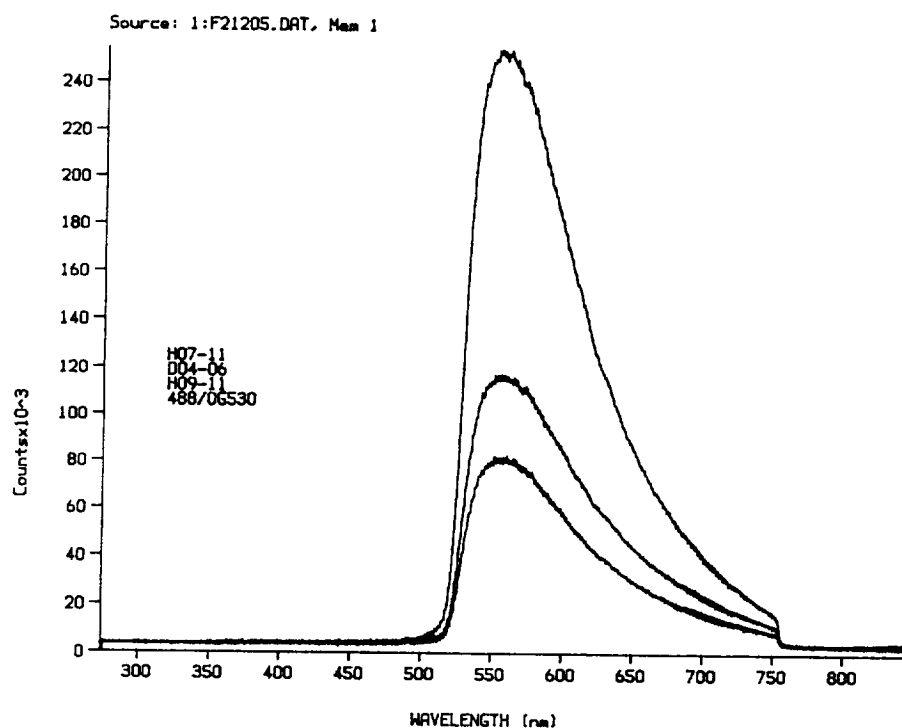
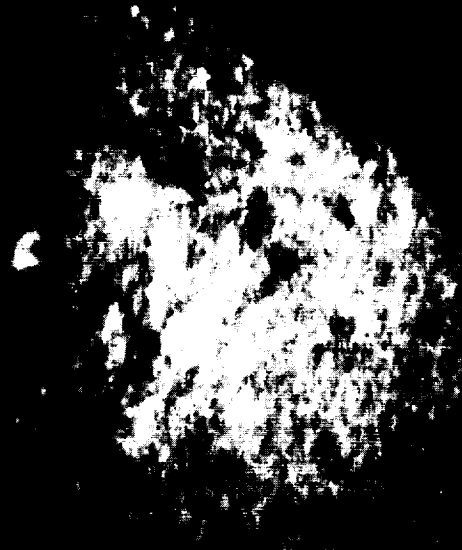


Figure 5. Laser-induced fluorescence spectra from the central reflective portion of three samples. (Upper curve is from H07-11, middle curve is from D04-06, lower curve is from H09-11.)

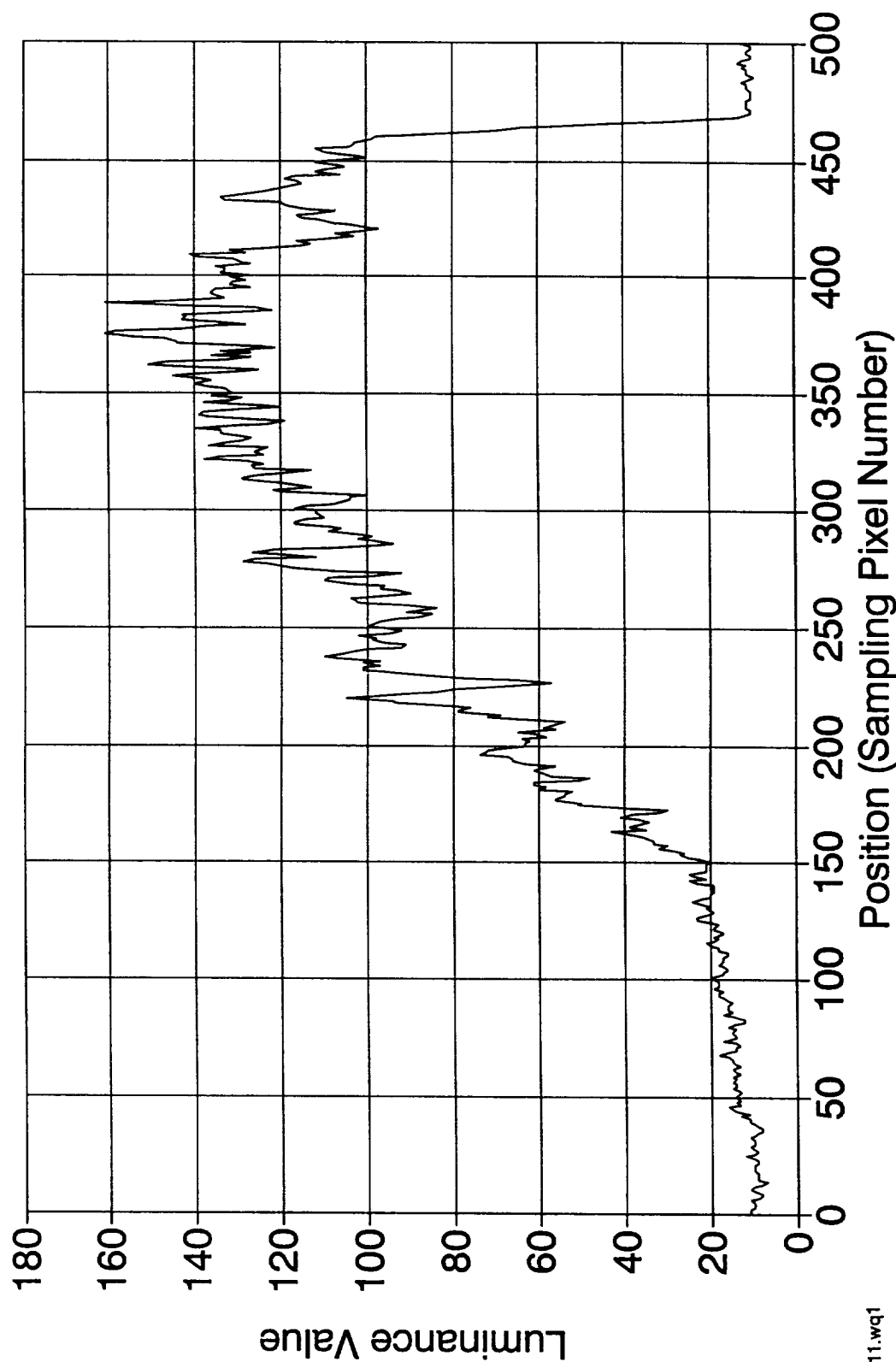
H07-11 LIF
488 nm/OG530/f12.5



Filename: PU322_01.TIF

Figure 6. Video image of integrated laser-induced fluorescence from sample H07-11. (Top of the picture corresponds to the 9 o'clock position on the sample. Note the saturated area on the image is possibly embedded fibrous debris.)

Laser-Induced Fluorescence 488/OG530 LDEF Tray Clamp H07-11



pu32211.wq1

Figure 7. Integrated laser-induced fluorescence line scan from the image in Figure 6. (Along a line from the 9 o'clock position on the sample to the 3 o'clock position, i.e., vertical scan on Figure 6.)